Electrolytic Reduction of Nitriles.

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(Received August 31, 1942.)

In order to study the electrolytic reduction of nitriles with platinum cathode covered with palladium, the present author attempted the reduction of typical compounds containing CN-group and found that they were readily reduced to the corresponding amines.

The electrolytic reduction of nitriles has been reported only by a few workers.[1] One example is described by Mr. T. Matukawa[2] in the case of 2-methyl-4-amino-5-cyano-pyrimidine, which is reduced in acidic solution with platinum cathode covered with palladium to 2-methyl-4-amino-5-aminomethyl-pyrimidine hydrochloride. The author applied this method to other compounds containing CN-group and found that they were comparatively readily reduced. Moreover, some nitriles, e.g., malonitrile, ethylenecyanohydrin, cyanoacetic acid, which are difficult to reduce by the ordinary reduction methods, could be readily reduced with electrolytic reduction.

In Table 1, the nitrile used, and their reduction products and yields are summarized. The reduction products were identified as free bases, hydrochlorides or their suitable derivatives by comparing their melting points or boiling points with what is described in the literature and by analysis.

Among these, the reduction of malonitrile and ethylenecyanohydrin have never been attempted, but by electrolytic reduction the author obtained trimethylenediamine hydrochloride and γ-oxypropylamine respectively. β-Alanine has been obtained by Hofmann's reaction from succimide[3], but by electrolytic reduction it can be readily obtained from cyanoacetic acid and it seems to be an excellent method of preparing β-alanine.

(1) K. Ogura, *Memoirs of the College of Science of Kyoto Imperial University*, **12**(1929), 339.

(2) T. Matukawa, *Jap. Pat.* No. 133464 (1939).

(3) Hoogewerff and Van Dorp, *Rec. trav. chim.*, **10**(1893), 4.

Table 1.

	Nitrile	Reduction products	Yield (%)
I	CH_3CN	$CH_3CH_2NH_2$	100
II	o-$CH_3 \cdot C_6H_4CN$	o-$CH_3 \cdot C_6H_4CH_2NH_2$	40
III	$C_6H_5 \cdot CH_2CN$	$C_6H_5 \cdot CH_2CH_2NH_2$	75
IV	$CN \cdot CH_2 \cdot CN$	$NH_2(CH_2)_3NH_2$	50
V	$CN \cdot CH_2 \cdot CH_2 \cdot CN$	$NH_2(CH_2)_4NH_2$	70
VI	$CN(CH_2)_4CN$	$NH_2(CH_2)_6NH_2$	40
VII	$CN \cdot CH_2 \cdot CH_2 \cdot OH$	$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$	30
VIII	$CN \cdot CH_2 \cdot COOH$	$NH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$	40

In the present experiments the author adopted nearly the same condition, but it is obvious that the condition of electrode, current density, concentration of acid in catholyte, temperature etc. have great influences on the yield, and it is expected that the yield described in Table 1 might be greately increased. Indeed, in some cases, the formation of ammonium chloride in the reduction products was observed. According to Braun,[4] the mechanisms of reduction of nitrile are formulated as follows:

$$\text{(A)}\quad R\text{-}CN + 2H \longrightarrow R\text{-}CH{:}NH \ \text{(IX)} \xrightarrow{+2H} R \cdot CH_2 \cdot NH_2 \ \text{(X)}$$

$$\text{(B)}\quad R\text{-}CH{:}NH + R \cdot CH_2NH_2 \longrightarrow R\text{-}CH\begin{matrix}\diagup NH_2 \\ \diagdown NH \cdot CH_2R\end{matrix} \ \text{(XI)} \xrightarrow[-NH_3]{+2H} R \cdot CH_2NHCH_2\text{-}R \ \text{(XII)}$$

Nitrile is at first reduced to aldimine (IX) which is further reduced to primary amine (X). (X) may react with the aldimine yielding an addition compound (XI), which is unstable and by further reduction and loss of ammonia produced secondary amine (XII). Hartung[5] reported that the formation of secondary amine can be suppressed by carrying out the reduction in the presence of hydrochloric acid which fixes the resulting primary amine as hydrochloride.

The author has also carried out the reduction in the presence of mineral acid; even when the formation of ammonium chloride was occasionally observed. Studies concerning the problem whether the formation of ammonium chloride is due to the above mentioned mechanisms or to the hydrolytic decomposition of nitrile are in progress.

Experimental.

General Procedure of Reduction. The apparatus for reduction consists of (i) a 200 c.c. beaker as an electrolytic bath; (ii) platinum wire net (150 $cm.^2$) as cathode; (iii) platinum wire as anode; (iv) a porous unglazed porcelain cylinder as a diaphragm. Preparation of cathode: A mixture of 50 c.c. of water, 10 c.c. of concentrated hydrochloric acid and a solution of 0.5–1 g. of palladium chloride in a little dilute hydrochloric acid are used as catholyte and electrolyzed at room temperature (current density: 0.02 amp./$cm.^2$). The colour of palladium chloride having disappeared, the catholyte was taken out and then reduction was carried out.

(4) v. Braun, *Ber.*, **56**(1923), 1988. Cf. T. Hoshino, *J. Soc. Chem. Ind. Japan*, **44**(1941), 1085.

(5) Hartung, *J. Am. Chem. Soc.*, **50**(1928), 3370.

A solution of a nitrile in dilute hydrochloric acid (when the nitrile was sparingly soluble in water, it was dissolved by adding glacial acetic acid) was used as catholyte and reduced electrolytically. The bath was cooled with ice water from outside. When the reduction was not smooth, a small amount of palladium chloride solution was added to the catholyte. Dilute hydrochloric acid was used as anolyte. After reduction the catholyte was taken out and evaporated to dryness in vacuum and the residual amine hydrochloride was identified as such or as a suitable derivative.

(I) Reduction of acetonitrile. Catholyte: 1 g. of acetonitrile was dissolved in 50 c.c. of 8% hydrochloric acid. Anolyte: dilute hydrochloric acid. Current density: 3 amp./dm.^{2}. Electrolysis was conducted at 15° for two hours. The electrolyte was taken out after electrolysis, and evaporated in vacuum. 2 g. of pure ethylamine hydrochloride was obtained. The yield was quantitative. The picrate melted at 169°.

(II) Reduction of *o*-tolunitrile. Catholyte: 1 g. of the nitrile was dissolved in a mixture of 50 c.c. of glacial acetic acid, 10 c.c. of concentrated sulphuric acid and a little water. Anolyte: 20% sulphuric acid. Current density: 2 amp./dm.^{2}. Temperature: 10.° After one hour and a half, the catholyte was concentrated in vacuum, made strongly alkaline with sodium hydroxide and extracted with ether. The ether extract was shaken with dilute hydrochloric acid. The hydrochloric acid solution was evaporated to dryness under reduced pressure. The residue was recrystallized from absolute alcohol by adding a little ether. 0.5 g. of *o*-tolubenzylamine hydrochloride was obtained, m.p. 217°. Found: N, 8.88. Calcd. for $C_8H_{12}NCl$: N, 9.07%.

(III) Reduction of benzylcyanide. Catholyte: 1 g. of benzylcyanide was disolved in a mixture of 30 c.c. of glacial acetic acid, 10 c.c. of water and 10 c.c. of concentrated hydrochloric acid. Anolyte: 10% hydrochloric acid. Current density: 2 amp./dm.^{2}. Temperature: 10°. After two hours the catholyte was treated as described in general procedure. 1 g. of phenylethylamine hydrochloride was obtained. Yield 75%; m.p. 217°. Found: C, 61.05; H, 7.67. Calcd. for $C_8H_{12}NCl$: C, 60.95; H, 7.62%.

(IV) Reduction of malonitrile. Catholyte: 1 g. of malonitrile was dissolved in a mixture of 40 c.c. of water and 10 c.c. of concentrated hydrochloric acid. Anolyte: dilute hydrochloric acid. Current density: 3.5 amp./dm.^{2} Temperature: 8–10°. After two hours' electrolysis the catholyte was evaporated under reduced pressure, the residue was fractionally crystallized from alcohol. 0.3 g. of ammonium chloride and 1.1 g. of trimethylenediamine hydrochloride (m.p. 243–4°) were obtained. Yield 50%. Found: N, 18.91. Calcd. for $C_3H_{12}N_2Cl_2$: N, 19.05%. Picrate: m.p. 216°, from dilute alcohol.

(V) Reduction of succinonitrile. Catholyte: 1 g. of nitrile was dissolved in 60 c.c. of 10% hydrochloric acid. Current density: 5 amp./dm.^{2} Temperature: 10°. After one hour's electrolysis, the catholyte was treated as in the reduction of acetonitrile. 1.4 g. of teramethylenediamine

hydrochloride was obtained, m.p. over 290°. Yield: 70%. Found: N, 17.27. Calcd. for $C_4H_{14}N_2Cl_2$: N, 17.33%.

(VI) Reduction of adiponitrile. The reduction was conducted under the same condition as in the reduction of succinonitrile. From 1 g. of the nitrile 0.7 g. (40%) of hexamethylenediamine hydrochloride was obtained, m.p. 246°. Found: N, 14,60. Calcd. for $C_6H_{18}N_2Cl_2$: 14.81%.

(VII) Reduction of ethylenecyanohydrin. Catholyte: 10 g. of ethylenecyanohydrin was dissolved in 90 c.c. of 7% hydrochloric acid. Current density: 4 amp./dm.^{2}. Temperature: ca. 10°. After nine hours' electrolysis, the catholyte was evaporated under reduced pressure and the residue was dissolved in absolute alcohol containing a little absolute ether. A small amount (0.9 g.) of ammonium chloride was filtered off and the filtrate was neutralized with alcoholic sodium hydroxide, filtered from sodium chloride and the solvent was distilled off. The residue was first distilled under reduced pressure. The fraction which distilled over at 105–110° under 25 mm. was redistilled under ordinary pressure. 3 g. (30%) of γ-hydroxypropylamine was obtained. The boiling point was 185–189°.[6] For the purpose of identification 1 g. of the hydroxyamine was dissolved in water, and shaken with 3 g. of phenylisocyanate. The reaction occurred instantly and white precipitate was produced. After ten minutes, the precipitate was collected and recrystallized at first from water, then from dilute alcohol, m.p. 140°. Found: N, 13.51. Calcd. for $C_6H_5NHCONHCH_2CH_2CH_2OCONHC_6H_5$: N, 13.41%.

(VIII) Reduction of cyanoacetic acid. Catholyte: 2 g. of cyanoacetic acid was dissolved in 60 c.c. of 10% hydrochloric acid. Current density: 2 amp./dm^2. Temperature: 8–10°. After 3 hours, the catholyte was evaporated under reduced pressure, the residue was dissolved in a small amount of absolute alcohol, and ether was added. 1 g. of β-alanine hydrochloride (m.p. ca. 120°) was obtained. It was identified as a phenylisocyanate derivative as follows: 1 g. of the product was dissolved in sodium hydroxide solution (0.7 g. NaOH) and shaken with 1 g. of phenylisocyanate. White precipitate which was instantly produced was collected and recrystallized from hot water, m.p. 171°. Analysis shows that this is the known γ-ureidopropionic acid[7]. Found: N, 13.55. Calcd. for $C_{10}H_{12}O_3N_2$: N, 13.46%.

In connection with this research the author expresses his sincere thanks to Dr. T. Hoshino for his kind guidance and also to Mr. H. Kawasumi for analysis and to Mr. C. Koyama for his collaboration in this research.

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(6) According to Henry, *Ber.*, **33**(1900), 3169 the boiling point of γ-hydroxypropylamine is 187–188°/756 mm.

(7) Hoogewerff and Van Dorp, *Rec. trav. chim.*, **9**(1890), 60.